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Dielectric Proof of the Photoresponse of Azo-Doped Silica-Nanostructured Liquid Crystal

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Abstract. We have examined the photoresponse of azo-doped silica-nanostructured liquid crystal (LC) by means of dielectric measurements through the electrical impedance spectroscopy. The studied material was the LC 4-n-heptyl cyanobiphenyl (7CB) that was nanostructured with 3 wt.% silica nanoparticles of size ~ 7 nm. This nanocomposite was photo-sensitized with the photoactive azobenzene LC 4-(4'-ethoxyphenylazo)phenyl hexanoate (EPH) at concentration of 3 wt.%. Upon exposure on low-intensity ultra-violet (UV) light, a clear increase in the room-temperature dielectric permittivity of the photoactive EPH-doped nanostructured LC was registered in the frequency range 0.5 Hz – 100 Hz. Thus, the electrical impedance spectroscopy was able to detect the UV-light-produced effect in considered photoactive nanomaterial resulting from *trans*-to-*cis* photoisomerization of EPH molecules (the photoactive nanodopants).

Keywords: Electrical impedance spectroscopy, dielectric permittivity, silica-nanostructured liquid crystals.

1. INTRODUCTION

The silica-nanostructured liquid crystals (LCs) (Kreuzer & Eidenschink, 1996; Iannacchione, 2004; Lobo et al., 2006; Bapat et al., 2010) have attracted significant research attention due to their interesting properties and prospective applications in electronic and electro-optical devices (Garbovskiy & Glushchenko, 2011). In most common case, they are fine dispersions of silica (SiO_2) nanoparticles in LCs. By adding of photoresponsive agent, one can make these nanocomposites photoactive.

Recently, a photoresponsive system formed from the LC heptylcyano-biphenyl (7CB) doped with 3 wt.% silica nanoparticles (aerosil nanospheres with a mean diameter ca. 7 nm) with addition of 3 wt.% of azobenzene LC 4-(4'-ethoxyphenylazo)phenyl hexanoate (EPH), was reported (Marinov et al., 2016). Being upon alternating-current (AC) electric field, this azo-doped silica-nanostructured system exhibits an ultra-violet (UV) light-induced enhancement of the voltage-dependent optical transmittance that is of interest for light-controllable electro-optics (Marinov et al., 2016).

The study presented here is focused on the characterization of this photoresponsive soft nanocomposite in terms of its dielectric properties. Thin films of EPH-doped aerosil/7CB were exposed on UV light at the wavelength of 375 nm and measured by electrical impedance spectroscopy. As reported previously (Marinov et al., 2016), such illumination leads to significant photoactivity of the EPH-doped aerosil/7CB nanocomposite due to efficient *trans-cis* photoisomerization of the azobenzene photoactive molecules of EPH. Our aim was to register the corresponding photo-induced dielectric changes in the examined photoactive nanomaterial.

2. THEORETICAL BASIS

Electrical measurements by Complex Electrical Impedance Spectroscopy (CEIS) were used to collect experimental data necessary to get dielectric characteristics of the EPH-doped silica-nanostructured 7CB LC material considered here. By the experimental technique CEIS (Barsoukov & Macdonald, 2005), both real (Z') and imaginary (Z'') parts of the complex electrical impedance (Z^*) can be simultaneously obtained as a function of the frequency f of the applied AC electric field.

From the frequency-dependent Z^*, one can calculate the real (ε') and imaginary (ε'') parts of complex dielectric permittivity $\varepsilon^*(f)$ by use of the following expressions (Barsoukov & Macdonald, 2005):

$$\varepsilon' = -\frac{Z''}{(Z'^2 + Z''^2)}\,\frac{d}{\varepsilon_0 A}\,\frac{1}{2\pi f} \tag{1}$$

and

$$\varepsilon'' = \frac{Z'}{(Z'^2 + Z''^2)}\,\frac{d}{\varepsilon_0 A}\,\frac{1}{2\pi f} \tag{2}$$

where d, ε_0 and A are, respectively, the film thickness, the vacuum permittivity and the electrically active area of the film surface.

3. DATA

The synthesis of the EPH-doped silica-nanostructured 7CB LC, the preparation of the films with a thickness of 25 μm from this nanomaterial, as well as other experimental details, have been described in (Marinov et al., 2016). The nanocomposite films with polyimide alignment layers were placed between two electrically-conductive and optically-transparent indium tin oxide (ITO)-coated glass plates that serve as electrodes. The samples were illuminated with continuous UV light (from light-emitting diode, LED, whose emission was at the wavelength λ = 375 nm). The UV-light intensity on the sample was ~ 3 mW/cm^2).

The characterization by CEIS was performed by modular potentiostat/galvanostat SP-200 Bio-Logic (Bio-Logic Science Instruments). This compact and powerful computer-controlled workstation for impedance spectroscopy incorporates the latest measurement technology, has excellent specifications and can be applied as perfect instrument in dielectric research. SP-200 offers floating mode, analog filtering, build-in calibration board and excellent electronic stability.

Fig. 1 reports raw data for the complex electrical impedance measured for considered films of azo-doped LC nanomaterial as a function of the frequency f of the external electric field (in our case, applied perpendicular to the film plane).

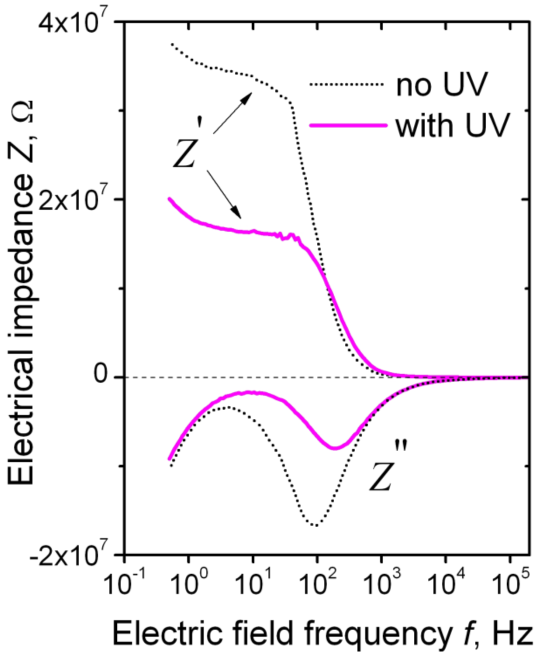

Fig. 1 Real (Z') and imaginary (Z'') parts of complex impedance measured for EPH-doped aerosil/7CB nanocomposite film: with no UV light (dotted); with UV light (bold lines). The emperature of the film was 24° C.

The impedance spectra were recorded in the frequency range f = 0.5 Hz – 200 kHz. The alternating-current (AC) electric field in the sinusoidal waveform was transversally applied to the film via the conductive ITO electrodes. The electrically active area of the sample was 0.38 cm^2. The applied voltage was kept fixed at 0.5 V (RMS). Thus, the corresponding electric field strength was smaller than the Freedericksz transition threshold of 7CB (equal to 0.96 V_{RMS}), thereby the electro-optical function of this LC was not activated. The experiment was carried out at ambient temperature.

4. METHODOLOGY

The photoresponse of the EPH-doped silica-nanostructured LC 7CB upon illumination with UV light was proven through the light-induced change of the dielectric properties of this nanocomposite. For the purpose, the frequency-dependent complex dielectric permittivity function of the studied material was calculated from the impedanciometer output (the recorded impedance spectra) by use of Eqs.1 & 2. This was done for the studied material exposed on UV light, and the same procedure was repeated under identical experimental conditions but with no illumination. Then the results from both measurements were compared.

5. EXPERIMENTAL RESULTS

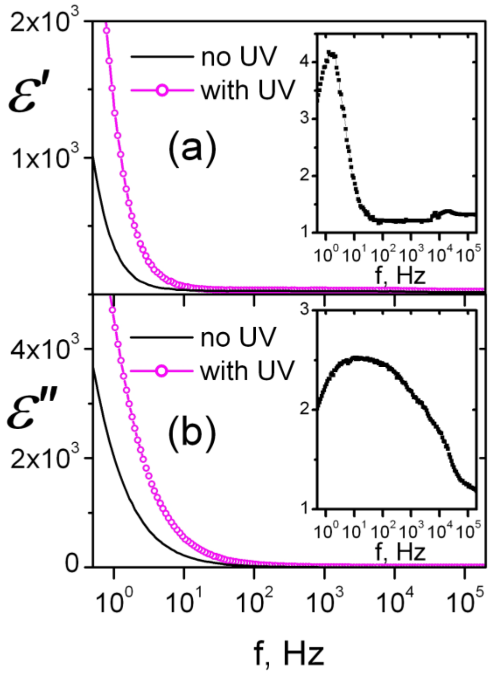

Fig. 2 Real (a) and imaginary (b) parts of frequency-dependent dielectric permittivity of EPH-doped aerosil/7CB nanocomposite film with and in absence of UV light. The insets: the UV-light-induced changes.

Fig. 2 shows the results for the calculated dielectric permittivity of the studied EPH-doped aerosil/7CB nanocomposite. The corresponding UV-light-induced effect on both dielectric characteristics (the ratio of their values with/without UV light at any frequency value within the measured range) is also given.

6. COMMENTS AND CONCLUSION

As compared to the non-illuminated case, a distinctly enhanced dielectric response (an increase of the dielectric permittivity values) of the azo-doped silica-nanostructured LC takes place upon UV light (Fig. 2). As seen, the UV-light-induced enhancement of ε'' (called the absorption or dielectric loss curve) is spread in larger range of frequencies than that of ε' (called the dispersion curve). Especially, the dielectric enhancement by illumination with UV light is well pronounced in the low-frequency region (in our case, 0.5 Hz – 100 Hz) (Fig. 2). This is an indicator of the photo-induced changes in the material under study. Actually these changes are the light-driven molecular conformation changes of the azo-bonded EPH molecules (Marinov et al., 2016).

The mechanism of geometrical and electronic modification through photochromic *trans-cis* photo-isomerization, is well known (Rau, 1990; Zhao & Ikeda, 2009), in particular, for EPH photoactive molecules (Prasad et al., 2005; Sridevi et al., 2011; Yelamaggad et al., 2012). The photoisomerization is a molecular property in which selective photoexcitation of the molecules causes transformation between isomers that are structurally different (in our case, the transition from rod-shaped *trans* isomers of EPH to its bent-shaped *cis* isomers by illumination with light in the UV spectral range, and corresponding change in the absorption – electronic spectra).

In fact, the nanomaterial considered here becomes more dipolar because the dipole moment of the azobenzene group is increased by *trans-cis* photoisomerization (Yager & Barrett, 2009). The UV light brings the azobenzenes from their *trans* form (benzene rings are opposite one another and have a dipole moment of ~ 0 D) to their *cis* form (benzene rings closer to one another and a dipole moment of ~ 3 D) (Yager & Barrett, 2009). Practically, this UV-light-induced large dipolar change predetermines the UV-light-induced change in dielectric response of EPH-doped aerosil/7CB nanocomposite studied here.

In conclusion, by CEIS we experimentally proved the UV-light-induced effect in the studied azo-doped silica-nanostructured LC. Actually, this effect was monitored by the change in the dielectric permittivity of the examined material (in our case, EPH-doped aerosil/7CB nanocomposite) assessed by using the impedance-meter output.

The information obtained for the dielectric characteristics can be further related to the photoresponse of considered azo-doped silica-nanostructured LC. Besides important material parameters like the static dielectric permittivity and electrical conductivity, the dielectric spectra can also provide information on the molecular dynamics and on the number of characteristic relaxation modes that can be associated with certain molecular rotations; the characteristic frequencies reflect how those motions are hindered. Such information is of importance when one considers the light-controllable electro-optic, photonic and sensor applications of photoactive LC nanomaterials.

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REFERENCES

Bapat P.N., Rao D.S.S., Prasad S.K. & Yelamaggad C.V., 2010. High-Pressure Dielectric Investigations of Nanocolloidal Aerosil-Nematic Liquid Crystal Composites, *J. Phys. Chem. B*, 114(40), 12825–12832.

Barsoukov E. & Macdonald J.R. (eds), 2005. *Impedance Spectroscopy: Theory, Experiment, and Applications*, 2nd edn, – John Wiley & Sons, Hoboken, NJ, USA.

Garbovskiy Y.A. & Glushchenko A.V., 2011. Liquid Crystalline Colloids of Nanoparticles: Preparation, Properties and Applications. In: Camley R.E. & Stamps R.L. (eds), *Solid State Physics*. 62. –Academic Press, Elsevier, New York, pp. 1–74.

Iannacchione G.S., 2004. Review of liquid-crystal phase transitions with quenched random disorder, *Fluid Phase Equlibria*, 222-223(15 Aug) 177–187.

Kreuzer M. & Eidenschink R., 1996. Filled Nematics. – In: Crawford G.P. & Zumer S. (eds), *Liquid Crystals in Complex Geomteries Formed by Polymer and Porous Networks*. – Taylor & Francis, London, UK, chapter 15, pp. 307–324.

Lobo C.V., Prasad S.K. & Yelamaggad C.V., 2006. Experimental investigations on weakly polar liquid crystal–aerosil composites, *J. Phys.: Condens. Matter*, 18(3), 767–776.

Marinov Y.G., Hadjichristov G.B., Petrov A.G. & Prasad S.K., 2016. Photo-controllable electro-optics of aerosil/7CB nanocomposite nematic doped with azo-bonded molecules, *J. Phys.: Conf. Ser.*, 682, 012030 (1-5).

Prasad S.K, Nair G.G, Hegde G., Sandhya K.L., Rao D.S.S., Lobo C.V. & Yelamaggad C.V., 2005. *Phase Transitions*, 78(6), 443–455.

Rau H., 1990. Photoisomerization of Azobenzenes. – In: Rabek J.F. (ed), *Photochemistry and Photophysics*, Vol. 2. – CRC Press, Boca Raton, FL, USA, chapter 4, pp. 119–142.

Sridevi S., Hiremath U.S., Yelamaggad C.V., Prasad S.K., Marinov Y.G., Hadjichristov G.B. & Petrov A.G., 2011. Behaviour of photosensitive soft materials: Thermo-optical, dielectric and elastic constant studies on azo-dye doped nematic liquid crystals, *Mater. Chem. Phys.*, 130(3), 1329–1335.

Yager, K.G. & Barrett C.J., 2009. Azobenzene Chromophores in Photo-Reversible Materials. – In: Zhao Y. & Ikeda T. (eds), *Smart Light-Responsive Materials: Azobenzene-Containing Polymers and Liquid Crystals*. – John Wiley & Sons, Boca Raton, FL, USA, chapter 1, pp. 1–46.

Yelamaggad C.V., Prasad S.K. & Li Q., 2012. Photo-Stimulated Phase Transformations in Liquid Crystals and Their Non-Display Applications. – In: Li Q. (ed), L*iquid Crystals Beyond Displays: Chemistry, Physics, and Applications*. – John Wiley & Sons, Hoboken, NJ, USA, chapter 5, pp. 155–211.

Zhao, Y. & Ikeda, T. (eds), 2009. *Smart Light-Responsive Materials: Azobenzene-Containing Polymers and Liquid Crystals*. – John Wiley & Sons, Hoboken, NJ, USA